

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C04B 7/02	A1	(11) International Publication Number: WO 93/21122 (43) International Publication Date: 28 October 1993 (28.10.93)
(21) International Application Number: PCT/DK93/00132 (22) International Filing Date: 13 April 1993 (13.04.93) (30) Priority data: 0495/92 13 April 1992 (13.04.92) DK (71) Applicant (for all designated States except US): AALBORG PORTLAND A/S [DK/DK]; Rørdalsvej 44, DK-9100 Aalborg (DK). (72) Inventors; and (75) Inventors/Applicants (for US only) : BORGHOLM, Hans, Erik [DK/DK]; H.C. Hansens Vej 8, DK-9210 Aalborg Ø (DK). DAMTOFT, Jesper, Sand [DK/DK]; Ravndal- en 73, DK-9310 Vodskov (DK). (74) Agent: PLOUGMANN & VINGTOFT A/S; Sankt Annæ Plads 11, P.O. Box 3007, DK-1021 Copenhagen K (DK).		(81) Designated States: CA, FI, NO, PL, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CEMENT COMPOSITION (57) Abstract A cement composition consisting essentially of: a) from 50 % to 97 % by weight (calculated on the total composition) of a Portland cement clinker, the sulfur content of which is in the range of 0.5-10 % by weight expressed as SO ₃ , and the fluorine content of which is in the range of 0.13-1.00 % by weight expressed as F ⁻ ; and b) from 3 % to 50 % by weight (calculated on the total composition) of an extender containing a carbonate selected from calcium carbonate, magnesium carbonate and calcium magnesium carbonate, and mixtures thereof, as its main constituent and having a median particle size (d ₅₀) of below 14 µm.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

CEMENT COMPOSITION**FIELD OF THE INVENTION**

The present invention relates to compositions of extended hydraulic cements, that is cements which, upon mixing with water set and harden to give substantial strength, and more particularly to extended cement compositions exhibiting high strength.

BACKGROUND OF THE INVENTION

The chemical parameters LSF, S/R and A/F referred to in this specification are:

$$\text{Lime Saturation Factor (LSF)} = \frac{\text{CaO} - 0.7 \text{ SO}_3}{2.8 \text{ SiO}_2 + 1.2 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3}$$

$$15 \quad \text{Silica Ratio (S/R)} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$$

$$\text{Alumina Ratio (A/R)} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$$

$$20 \quad \text{Sodium oxide equivalent (Na}_2\text{O}_{\text{eq}}) = 0.658 \cdot \text{K}_2\text{O} + \text{Na}_2\text{O}$$

In the foregoing ratios, the chemical symbols represent percentage by weight of the identified substance present in the composition. In the following description and claims the percentages referred to are by weight.

25 Four cement minerals are usually regarded as the major constituents of Portland cement clinker: Alite which mainly consists of tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) designated C_3S , belite which mainly consists of dicalcium silicate

($2\text{CaO}\cdot\text{SiO}_2$) designated C_2S , tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) designated C_3A , and tetracalcium aluminate ferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) designated C_4AF .

Throughout this specification, the quantity of the main
5 clinker compounds have been calculated according to the Bogue
formulas, corrected for the presence of SO_3 in the clinker
(F.M. Lea: "The Chemistry of Cement and Concrete." Edward
Arnold (Publishers) Ltd., London, p. 115-116). It is also
possible to determine the content of C_3S directly by quanti-
10 tative X-ray diffraction, although it is necessary to apply a
correction allowing for the increased C_3S content due to the
solid solution of Al, Fe, F, Mg, and other elements into the
 C_3S in order to obtain results that can be compared with the
 C_3S content calculated according to Bogue.

15 A number of minor components such as MgO , TiO_2 , Mn_2O_3 , K_2O
and Na_2O are present in the clinker although they usually do
not amount to more than a few percent of the cement. Two of
the minor components are of particular interest: sodium oxide
(Na_2O) and potassium oxide (K_2O) also known as the alkalis
20 (although other alkali metals also exist in cement). They
have been found to react with some aggregates by an expansive
reaction, the so-called alkali-aggregate reaction. The pro-
ducts of this reaction may cause disintegration of the con-
crete, and necessitate costly repair or even demolition of
25 structures.

It has been found that expansion due to alkali-aggregate
reaction can be reduced or eliminated by the use of cement
with low alkali content. In several countries the use of
cement with high alkali content is therefore restricted by
30 standards, recommendations and other regulations. For exam-
ple, in Denmark the alkali content of cement should pre-
ferably be less than 0.8% sodium oxide equivalent to be used
for ready mixed concrete and for concrete element production.
For other applications, even lower alkali contents are pre-

ferred. Generally, it is desirable that the alkali content should be as low as possible.

Portland cement is typically manufactured by a process, according to which clinker is obtained by heating to partial fusion a mixture comprising limestone and a combination of various materials containing the necessary quantities of silica, alumina and iron oxide, such as sand, shale, clay or fly ash. The burning process is typically performed in a rotary kiln. The clinker is finely ground in a mill to obtain the finished Portland cement. Minor amounts of gypsum or other retarders are typically added to the mill in order to control the setting behaviour of the cement.

Cement production is a very energy-intensive process. Considerable energy is required to decompose CaCO_3 to CaO and CO_2 , to heat the clinker to the required sintering temperature of typically $1450\text{--}1550^\circ\text{C}$, and to grind the clinker to the required cement fineness. Furthermore, if wet raw materials are used, significant amounts of energy are spent evaporating the water.

Various gases, which may be undesirable from an environmental standpoint, are emitted during the production of Portland cement. The high temperatures involved results in the emission of nitrous oxides, and combustion of fuel and decomposition of limestone leads to significant release of CO_2 .

It is both from economical and environmental points of view desirable to reduce the energy consumption. The efforts to achieve this goal in the cement industry have mainly followed two lines:

- the use of mineralisers to reduce the sintering temperature
- the use of extenders to decrease the amount of the clinker consumed.

In cement making, the term mineraliser is used to describe substances that facilitate the sintering reactions that take place in the kiln. These substances may be added to the raw mix or may be inherent in the raw materials at certain locations. Fluxes are substances that increase the quantity of liquid phase during the sintering of the clinker, thus facilitating the formation of the clinker compounds.

Mineralisers containing fluorine such as calcium fluoride, aluminum fluoride and silicofluorides are the most studied types of mineralisers. The mineralising action may be attributed to several factors including increase of the alite formation rate, lowering of alite formation temperature and stabilization of alite crystals due to solid solution of fluoride in the alite crystals. However, it is well documented in the literature that the hydraulic activity of cements at early ages is reduced at high levels of fluoride additions.

Substances containing sulfur such as calcium sulfate and alkali metal sulfates may act as fluxes, but calcium sulfate is known to raise the temperature by which CaO and C_2S is combined to form C_3S .

Use of a combined mineraliser containing fluorine and sulfur is described in several references. These indicate that fluorine overcomes the undesirable effect of calcium sulfate mentioned above.

Reductions of the required sintering temperature of up to 200°C have been reported by use of the mentioned mineralisers. As heat is very effectively recovered in modern cement kilns, the potential energy savings are, however, relatively small; less than 5% for a 200°C reduction in burning zone temperature. However, an important benefit of the decreased burning temperature is a significant reduction in the emission of nitrous oxides.

A well-known method of producing less costly hydraulic binders is to substitute a part of the Portland cements with a so-called extender. An extender is a fine grained material with a median grain size similar to or finer than the Portland cement. Typical examples of extenders are ground limestone, natural pozzolana, pulverized fly ash (PFA), and blast furnace slag (BFS).

Although the extenders may contribute to the strength development, the dilution of the Portland cement component in the extended cements generally leads to inferior early and late strength compared with pure Portland cements. The strength of extended cements may to a certain extent be increased by milling the Portland cement component to a finer grain size which, however, results in higher milling costs and limits milling capacity. The late strength may be increased by selecting particularly reactive extenders such as certain blast furnace slags or natural pozzolana. The availability of these materials are, however, limited in many geographical regions.

Combining mineralised cement, i.e. cement produced by the use of mineralisers, with an extender could be a promising way of obtaining significant reductions of energy consumption and emission of CO₂ and nitrous oxides.

GB 1 498 057 (U.S. patent 4,042,408) describes cements produced by the use of mineralisers containing fluorine and sulfur. The main advantage of the use of mineralisers described in GB 1 498 057 is not the decreased sintering temperature, but that the use of mineralisers enables the manufacture of cements with high alite contents and hence high early and late strength. The early strength of the cements described in GB 1 498 057 is further enhanced by a considerable alkali content of the clinker.

It is reported in GB 1 498 057 that some of these cements are useful for incorporating with a pulverised fly ash or a blast

furnace slag extender, since the higher strength of the clinker in comparison with conventional Portland cement permit a larger addition of these extenders while achieving the same strength properties of the final mixture. The strength contribution of the extenders in question to the strength of the final mixture is, however, not improved by using the cement clinker described in GB 1 498 057 as base instead of conventional Portland cements. Thus, the dilution effect will tend to decrease the strengths of the extended cements based on the cements described in GB 1 498 057 in the same manner as extended cements based on conventional Portland cement. Consequently, combining the cement clinker described in GB 1 498 057 with fly ash or blast furnace slag is not the optimum method for producing inexpensive high strength cement compositions. Furthermore, the enhanced alkali content of the cements described in GB 1 498 057 limits their usefulness as base for extended cements because of the previously mentioned alkali-aggregate reaction.

For these reasons, it will be evident that an extended cement with production costs equal to or lower than conventional extended cements, but possessing early and late strength comparable to or higher than pure conventional Portland cement, would benefit numerous applications, in particular if the extended cement is of low alkali content. Very significant reductions of the clinker content of concrete might be achieved, both by the use of extended cement and by taking advantage of the high cement strength to reduce the cement content of the concrete without compromising concrete strength. Thus, significant reductions of cost, the amount of fuel needed, and the emission of nitrous oxide and CO₂ could be attained. A further benefit of such an extended cement would be that cement production capacity could be increased without the need for investment in costly equipment because a substantial amount of clinker could be substituted by an extender while the cement maintained the strength properties of a conventional Portland cement.

From the above it can be seen that there is a substantial need for an extended cement, in particular one whose clinker portion has a low alkali content, which on the one hand may be produced at reduced costs and with reduced emissions of CO₂ and nitrous oxides but on the other hand has high early and late strength and may make it possible to increase production capacity without the need for costly investments.

SUMMARY OF THE INVENTION

It has been found that the above needs can be substantially fulfilled by an extended cement composition, said composition consisting essentially of

- a) from 50% to 97% by weight (calculated on the total composition) of a Portland cement clinker, the sulfur content of which is in the range of 0.5-10% by weight expressed as SO₃, and the fluorine content of which is in the range of 0.13-1.00% by weight expressed as F⁻; and
- b) from 3% to 50% by weight (calculated on the total composition) of an extender containing a carbonate selected from calcium carbonate, magnesium carbonate and calcium magnesium carbonate, and mixtures thereof, as its main constituent and having a median particle size (d₅₀) of below 14 μm.

Ground limestone has found a certain application as extender for extended cements because of its low price and wide availability. It has also been observed that finely divided calcium carbonate may, in a limited way, contribute to the early strength development of extended cements when used together with conventional Portland cement clinker. This has been ascribed to the carbonate-containing extender perhaps acting as a fine filler filling out the voids between the larger particles or the material perhaps accelerating the hydration rate of the cement. However, finely divided calcium carbonate is generally regarded as a basically inert filler when used in extended cements. The early and late strengths of conven-

tional Portland cement extended with ground limestone are consequently limited.

It has now surprisingly been found that the fine carbonate-containing extender described above under b) provides a far
5 larger contribution to the strength development of extended cements based on the mineralised Portland cement clinker described under a) than to similar extended cements based on conventional Portland cement clinker. The enhanced strength contribution is at its maximum after 1 day but is for some
10 clinker compositions still very significant after 28 days.

By using the high strength potential of the Portland cement clinker described under a) in combination with the above described enhanced strength-contributing effect of the fine carbonate extender to said Portland cement clinker, surpris-
15 singly high strengths may be obtained by adding as much as up to 50% of the fine carbonate extender to the clinker. Preferred embodiments of the cement composition of the invention provide 1 and 28 day strengths which are similar or superior to comparable conventional Portland cements.

20 DETAILED DESCRIPTION OF THE INVENTION

In the cement composition of the invention, it has been found that the effect of the extender on the final strength of the hydrated composition increases with decreasing particle size of the extender. Consequently, it is preferred that the
25 median particle size (d_{50}) of the extender is below 12 μm , preferably below 10 μm , more preferably below 6 μm , in particular below 4 μm , especially below 3 μm .

The extender may in principle be selected from any type of rocks, mineral or synthetic compound or material containing
30 calcium carbonate, magnesium carbonate or calcium magnesium carbonate, or mixtures thereof. Examples which, however, are not in any way to be construed as exhaustive, include calcite, aragonite, dolomite, limestone, dolostone, dolomitic

limestone, travertine, calcarenite, coquina, chalk, marble, as well as industrial products, by-products or wastes containing such materials. The choice of the extender source may be affected by local availability.

- 5 One material which has been found to be very useful is carbonate-containing electrostatic precipitator dust resulting from flue gas cleaning in various industrial processes, in particular electrostatic precipitator dust extracted from cement kiln exhaust gases after the gases have passed through
10 a drier/crusher and a de-dusting cyclone, such materials typically consisting of finely divided chalk with minor amounts of fly ash and fine-grained sand.

As indicated above, calcium carbonate, magnesium carbonate or calcium magnesium carbonate as well as mixtures thereof
15 should be the main constituent of the extender. In the present context, the term "main constituent" is intended to mean that the carbonate(s) in question are present in an amount higher than any other single constituent in the extender. However, for the purposes of the present invention, it is
20 considered advantageous if the content of calcium carbonate, magnesium carbonate, calcium magnesium carbonate or mixtures thereof in the extender is at least 50%, preferably at least 60%, more preferably at least 70%, in particular at least 75%, more particularly at least 80% by weight, especially at
25 least 85% by weight, such as at least 95% by weight, calculated on the extender. The above discussed cement kiln electrostatic precipitator dust may typically (although dependent on the design and operation of the kiln) contain approximately 85% by weight of calcium carbonate, approx. 10% by
30 weight of fly ash, and approx. 5% by weight of fine sand.

With respect to the amount of the mineralised Portland cement clinker and extender in the composition of the invention and to achieve an optimum between strength and extender content, a preferred embodiment contains 60-95% by weight of cement
35 clinker and 5-40% by weight of the extender, in particular

65-95% by weight of cement clinker and 5-35% by weight of the extender, especially 70-90% by weight of cement clinker and 10-30% by weight of the extender.

The mineralised Portland cement clinker used in the composition of the invention preferably has a total content of C_3S and C_2S of at least 65%, more preferably at least 70%, in particular at least 75%, especially at least 80%, calculated according to Bogue and corrected for the content of calcium sulfate in the clinker.

- 10 In the composition of the invention, it is for reasons of ease of control of the clinker kiln preferred that the Portland cement clinker in the composition has a sulfur content in the range of 1.3-10% by weight expressed as SO_3 , and a fluorine content in the range of 0.13-0.55% by weight expressed as F^- ;
- 15 pressed as F^- ; the sulfur content expressed as SO_3 is advantageously in the range of 1.5-6% by weight, preferably 1.6-5%, in particular 1.8-4%, and the content of fluorine expressed as F^- is advantageously in the range of 0.15-0.45% by weight, preferably 0.15-0.35%, in particular 0.18-0.30%.
- 20 In order to limit the above described alkali/aggregate reactions, it is preferable if the alkali metal content of the clinker expressed as Na_2O equivalent is in the range of 0.1-8% by weight, preferably 0.2-0.7% by weight, more preferably 0.3-0.6% by weight.
- 25 In order to improve the strength of the composition containing the cement clinker used in the composition of the invention, it is advantageous if the C_3S is of improved hydraulic activity, i.e. present in the crystal modification characterized by the presence in the X-ray diffractogram of only
- 30 one peak in the region 51° - 52° 2θ corresponding to the 220 reflection of the hexagonal subcell. In the present context, the term "improved hydraulic activity" is intended to mean that the hydraulic activity of the C_3S is enhanced relative to C_3S in conventional Portland cements.

Also, in order to increase the content of C_3S in the cement clinker for the propose of increasing the early strength of the composition, it is preferred that the fluorine in the Portland cement clinker is predominantly present in solid solution in the silicate crystal phases. In particular, it is preferred that at least 85% of the fluorine is present in solid solution in the silicate crystal phases of the clinker. For the same reasons, it is also advantageous if some aluminium is incorporated in solid solution in the silicate crystal phases, preferably that the silicate crystal phases contain more than 0,6% by weight of aluminium, calculated as Al_2O_3 , in particular more than 1.0%, especially more than 1.4%.

Since the lime saturation factor (LSF) of the Portland cement clinker used in the composition of the invention, when corrected for the content of calcium sulfate, is of significance for the content of C_3S in a cement clinker during the production thereof, it is preferred that the LSF is at least 0.95, preferably at least 0.97, in particular at least 0.99.

It is further normally useful that the silica ratio of the mineralised Portland cement clinker is in the range of 2-30, preferably 2-20, more preferably 3-20, in particular 4-20, especially 5-20, such as 5-15. However, it has surprisingly turned out that although compositions of the invention, the cement clinker of which have a high (e.g. above 6.5) silica ratio, generally exhibit a higher 1-day strength than similar compositions whose cement clinker portion has a relatively low (e.g. 2.3-2.8) silica ratio, compositions with low-silica ratio clinker have been shown to result in 28-day strengths comparable to those containing high-silica ratio clinker. Thus, the strength contribution of the fine carbonate-containing extender after 28 days is larger to the low-S.R. clinker than to the high-S.R. clinker, cf. the examples. Consequently, the choice of silica ratio in the cement clinker portion of the composition of the invention should be selected in view of these relationships.

It is also preferred that the sulfur/fluorine ratio expressed as SO_3/F in the Portland cement clinker is at least 6.6, preferably at least 7, in particular at least 8.

As mentioned previously, the composition of the Portland cement clinker in the composition of the present invention preferably exhibits a fairly high total content of C_3S and C_2S . However, it is further preferred that the content of C_3S in the clinker is at least 60%, more preferably at least 65%, in particular at least 70%, especially at least 75% by weight. These percentages are the contents determined based on the elemental composition of the cement according to Bogue.

In view of the desired silica ratios described above as well as the desire to incorporate aluminium into the alite crystals as a solid solution, it is advantageous that the content of Al_2O_3 in the Portland cement clinker of the invention is less than 6% by weight, preferably less than 5%, in particular less than 4%. but preferably larger than 0.5%, in particular larger than 1%. Also, it is preferable that the content of free lime is less than 3%, in particular less than 2% by weight in order to maximise the content of C_3S .

It is further preferred that the content in the clinker of calcium sulfate as dead-burned anhydrite is at least 0.1%, preferably at least 0.5%, more preferably at least 1%, in particular at least 2% by weight. However, in order to maintain the best possible set-regulating effects of the calcium sulfate included in the raw material, it is preferred that the content of calcium langbeinite is in the range of 0.1-8.3%, in particular 0.1-4% by weight of the clinker.

Since the compressive strength obtainable by hydrating a cement clinker is in part a result of the specific surface area of the ground cement clinker in that an increase in the specific surface area results in an increase of the strength development rate, it is preferred that the Portland cement

clinker in the composition of to the invention is provided in a form where it has been ground to a specific surface area according to Blaine of 150-1000 m²/kg, preferably 200-900 m²/kg.

- 5 The composition of the invention may advantageously further contain a retarding agent which may be any of the well-known retarding agents used in cements and cement compositions, such as calcium sulfate or hydrates thereof.

- 10 In order to keep the alkali metal content low in the composition of the invention, it is preferred that the carbonate-containing extender has an alkali metal content of below 0.8% by weight expressed as Na₂O equivalent.

- It is preferred that the cement composition of the invention is composed so that when the clinker is ground to a specific surface area according to Blaine of 400 m²/kg, the composition provides a 1-day compressive strength, when measured according to EN-196-1, of at least 21 MPa, more preferably at least 24 MPa, in particular at least 26 MPa, especially at least 28 MPa, such as 30 MPa. Likewise, it is preferred that 15 it provides a 28-day compressive strength, when measured according to EN-196-1, of at least 55 MPa, more preferably at least 60 MPa, in particular at least 65 MPa.

- The clinker used in the composition of the invention may be obtained commercially or may be manufactured by a classical 25 process comprising heating to partial fusion a mixture comprising principally lime and silica together with a smaller proportion of alumina and iron oxide in the presence of mineralisers comprising sulfur and fluorine under such conditions that the clinker will retain sulfate in an amount of 0.5-10% 30 by weight expressed as SO₃, and fluoride in an amount of 0.13-1.00% by weight. Such preparation may be carried out in a manner known per se to the person skilled in the art.

The process is preferably carried out in a rotary cement kiln. Several types of rotary kilns may be used, e.g. a wet process kiln, a long dry process kiln, a semi-wet process kiln, a semi-dry process kiln, a preheater cement kiln, or a
5 precalciner cement kiln. An added benefit of the use of mineralisers in the preparation of the Portland cement clinker in the composition of the invention is a reduction of the emission of nitrogen oxides compared with the preparation of clinker with a similar high C_3S content, but without the use
10 of mineralisers.

The fluorine-containing mineraliser components used in the raw material may be selected from fluorspar, fluorite as well as various fluorine-containing industrial byproducts. The sulfur-containing mineraliser may be selected from calcium
15 sulfate, calcium sulfite, or hydrates thereof, pyrite or any other suitable sulfur-containing natural or industrial raw material. Sulfate may also be introduced into the kiln as part of the fuel (e.g. by using sulfur-containing fuel).

The carbonate-containing extender may be added at the cement
20 plant before milling, during milling or after milling of the Portland cement clinker component described above. The carbonate-containing extender may also be mixed with cement based on the clinker described above, said mixing taking place outside the cement plant, for example at a construction site, or
25 the carbonate-containing extender and the cement may be added separately when mixing the intended paste, mortar or concrete. In such cases, the extender may be added as a dry powder or as a slurry, either separately or premixed with other constituents such as filler, sand, aggregate, other extenders
30 such as fly ash, silica fume or blast furnace slag, blending water, or various chemical additives.

In view of the above, the invention further concerns a composition comprising an extended cement composition as described above as well as one or more further components selected from
35 any of the commonly used or well known cement paste, mortar

or concrete additives or mixing materials used in cement technology. In this connection, reference is made to standard works in the field such as "Betonbogen", 2. Ed., 1985, Aalborg Portland, and Christian F. Justesen, "Tilsætningsstoffer
5 til Beton", Beton-teknik, 1/07/1983, Aalborg Portland.

Typical, but not limiting, examples of such additives are cement extenders, fillers, aggregate, plasticizing and super-plasticizing agents, accelerators, concrete retarders, air
10 entraining agents, defoaming agents, freezing point decreasing agents, adhesiveness improving agents, water repellants or waterproofing agents, expansion-promoting agents, corrosion inhibiting agents, radiation shielding agents, thickeners, as well as water for hydration.

As non-limiting examples of extenders may be mentioned silica
15 fume, calcined clay, natural pozzolan (e.g. volcanic ash, moler or diatomite), artificial pozzolan (e.g. fly ash, calcined moler, calcined diatomite or calcined clay), iron blast furnace slag, alumino-silicate, amorphous silica, rock flour, alumina, fluorspar, or mixtures thereof. As mentioned
20 above, the particle size of an extender is typically of the same order as that of the cement clinker in the composition which the extender is to be added to.

Non-limiting examples of aggregate are sand, gravel, crushed stone, crushed rock (such as granite, gneiss, limestone,
25 dolomite, marble, shale, slate, or schist), blast furnace slag, combustion slag, heavyweight aggregate (such as barytes, magnetite, limonite, ilmenite, iron or steel), lightweight aggregate (such as expanded clay, sintered clay, shale, slate, diatomaceous slate, perlite, vermiculite, slag,
30 natural pumice, scoria, volcanic cinders, tuff, diatomite, sintered fly ash, or industrial cinders), or mixtures thereof.

Typical but non-limiting examples of plasticizing agents are polyhydroxycarboxylic acids or salts thereof, lignosulfonates, polyethylene glycols, or mixtures thereof.

The superplasticising agent may typically be selected from
5 alkaline or earth alkaline metal salts of lignin sulfonates;
alkaline or earth alkaline metal salts of highly condensed
naphthalene sulfonic acid/formaldehyde condensates; alkaline
or earth alkaline metal salts of melamine/formaldehyde/sul-
fite condensates; sulfonic acid esters; carbohydrate esters;
10 or mixtures thereof.

The accelerator may typically be selected from soluble chlo-
ride salts (such as calcium chloride), triethanolamine, para-
formaldehyde, soluble formate salts (such as calcium for-
mate), sodium hydroxide, potassium hydroxide, sodium carbona-
15 te, sodium sulfate, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, sodium sulfate, and mix-
tures thereof.

Typical examples of the retarder are lignosulfonates, hydro-
xycarboxylic acids (such as gluconic acid, citric acid, or
salicylic acid), sugars, phosphates, borates, silico-fluo-
20 rides, calcium bromate, calcium sulfate, sodium sulfate, and
mixtures thereof.

As non-limiting examples of the air-entraining agent may be
mentioned vinsol resins, sodium abietate, fatty acids and
salts thereof, tensides, alkyl-aryl-sulfonates, phenol eth-
25 oxyates, lignosulfonates, and mixtures thereof.

Typical defoaming agents may be selected from silicones (such
as dimethylpolysiloxane), alkyl phosphates (such as tributyl
phosphate), and mixtures thereof.

In the composition, the freezing point decreasing agent is
30 typically selected from ethyl alcohol, calcium chloride,
potassium chloride, and mixtures thereof. The adhesiveness-

improving agent may typically be selected from polyvinyl acetate, styrene-butadiene, acrylics, and mixtures thereof.

The water-repellent or water-proofing agent may be selected from fatty acids (such as stearic acid or oleic acid), lower alkyl fatty acid esters (such as butyl stearate), fatty acid salts (such as calcium or aluminium stearate), silicones, wax emulsions, hydrocarbon resins, bitumen, and mixtures thereof.

Examples of expansion-promoting agents are aluminium powder, zinc powder, iron powder, calcium sulfoaluminate, and mixtures thereof. Corrosion-inhibiting agents may be selected from sodium nitrite, sodium sulfite, sodium chromate, and mixtures thereof. A radiation-shielding agent may be a boron compound, and a thickener may be a polyethylene oxide.

Water/cement (W/C) ratios may be from 0.15 (for ultra-dense materials such as those using high amounts of silica fume filler, e.g. materials of the Densit® type) up to 1.20, normally from 0.4 to 1.0, calculated on the extended cement.

The invention is further illustrated by the following non-limiting examples.

In the examples, chemical analysis and grain size distribution measurements of the cements were done by standard methods. Mineralogical compositions were calculated from the chemical analysis by use of the Bogue formulas corrected to allow for the presence of CaSO_4 in the cement (F.M. Lea: "The Chemistry of Cement and Concrete". Edward Arnold (Publishers) Ltd., London, p. 115-116).

Setting time and standard consistency were determined according to the European Standard EN 196-3, and the fineness (Blaine specific surface area) according to EN 196-6. The compressive strengths were measured according to either the Danish Standard DS 427 or EN 196-1. The only difference between these two standards resides in the method of compac-

ting the mortar during casting, and the results obtained are equivalent.

Characterization of the materials used in the examples are given in the tables below.

- 5 Table 1 shows the data of the base cements used. All cements were produced from clinker burned in production cements kilns. Gypsum was, in some cases, added to the mill during cement grinding. The approximate quantity gypsum added to the mill is indicated in Table 1. The reference conventional
10 Portland cements "X" and "Y" were produced from conventional Portland cement clinker. Cement "X" was manufactured by grinding the clinker in a laboratory cement mill equipped with a high efficiency separator. Cement "Y" was a commercially available conventional Portland cement (Aalborg Port-
15 land's "Rapid-Cement").

The data of the extenders used in the experiments are found in Table 2.

- The cement kiln electrostatic precipitator dusts "K", "L", and "M" were obtained from a semi-wet process precalcining
20 cement kiln. The dust was extracted by the electrostatic precipitator from the kiln flue gas after passing a drier crusher and a de-dusting cyclone. Electrostatic precipitator dusts "K" and "L" were obtained while the kiln was producing conventional Portland clinker, whereas dust "M" was obtained
25 while the kiln was producing mineralised clinker, hence the raised content of SO_3 and F. The cement kiln electrostatic precipitator dust "R" was extracted from the flue gases from a wet process cement kiln.

- The fine chalk "N" is a commercial product ("Alpine Fin" from
30 Dankalk, Denmark) produced by air classifying crushed chalk. The material has a grain size distribution similar to that of the electrostatic precipitator dust.

Coarse limestone "O" is a commercially available ground Danish limestone ("Grenå Foderkalk", from Faxe Kalk, Denmark), whereas coarse limestone "P" is a laboratory ground English limestone.

- 5 Fly ash "Q" (from a Danish coal-fired power station), the high-activity ground granulated blast furnace slag "S" (from Civil & Marine Slag, UK), and alumina "T" (CT-2000SG, from Alcoa, Germany) are all commercial products.

- 10 Throughout the examples both absolute and relative compressive strength of the extended cements tested are stated. The relative strengths are obtained by dividing the absolute compressive strength of the extended cement with the compressive strength of the matching base cement.

EXAMPLE 1

- 15 Mineralised cement "A" was produced by adding gypsum and fluorspar to the raw mix, burning the mixture in a production cement kiln, and grinding the clinker in a production cement mill circuit equipped with a high efficiency separator. No gypsum was added to the mill.
- 20 As a reference, conventional Portland cement "X" was used.

- Ca. 5 kg batches of blended cements were prepared by mixing the base cement with various amounts of cement kiln electrostatic precipitator dust "K" (median grain size: 2.5 μm), fine chalk "N" (median grain size: 2.1 μm), or coarse limestone "O" (median grain size: 9.6 μm), respectively. Mixing
25 was carried out by stirring the materials in a plastic container filled with rubber balls, using a shaking apparatus.

The results of the investigation are shown in Table 3.

The example illustrates the high 1-day strength which may be obtained by combining the carbonate-containing extender with a mineralised cement with a high silica ratio (S.R. = 7.0). The highest strengths are reached when cement kiln electrostatic precipitator dust "K" is used as the extender. The strength-contributing effect of the extender with the high-S.R. cement is apparently higher after 1 day than after 7 or 28 days.

EXAMPLE 2

- 10 Mineralised cement "B" was produced by adding gypsum and fluorspar to the raw mix, burning the mixture in a production cement kiln, and grinding the clinker in a laboratory cement mill equipped with a high efficiency separator. Ca. 0.9% by weight SO_3 was added as gypsum to the mill in order to reach
15 the specified cement SO_3 -content of 3.5% by weight.

As a reference, conventional Portland cement "X" was used.

- Ca. 5 kg batches of blended cements were prepared by mixing the base cement with various amounts of cement kiln electrostatic precipitator dust "L" (median grain size: 2.4 μm),
20 coarse limestone "P" (median grain size: 12.0 μm), fly ash "Q", or blast furnace slag "S", respectively. Mixing was carried out by stirring the materials in a plastic container filled with rubber balls, using a shaking apparatus.

- The results of the investigation are shown in Tables 4, 5a
25 and 5b.

- The tables compare a high-S.R. mineralised cement ("B", S.R. = 6.6) with a conventional cement ("X") as base for extended cements. The enhanced strength contribution of cement kiln electrostatic precipitator dust "L" or coarse
30 limestone "P", and the high strengths obtainable in combination with mineralised cement "B" is illustrated in Table 4.

The effect is more pronounced for the fine-grain electrostatic precipitator dust "L" than for the coarse limestone "P" and is most significant at the earliest ages. After 28 days, the strength contribution of the carbonate-based extenders
5 are similar regardless of cement type.

Table 5a illustrates that the relative strength contributions of fly ash "Q" or blast furnace slag "S" are fairly independent of the cement type. The strength contributions of fly ash and blast furnace slag are lower than those of the carbonate-based extenders combined with mineralised cement after 1
10 and 7 days. The strength contributions of fly ash are similar to those of the carbonate-based extenders combined with mineralised cement after 28 days.

Combinations of cement kiln electrostatic precipitator dust
15 "L" with fly ash "Q" or blast furnace slag "S", respectively (Table 5b), results in strength contributions intermediate between the results shown in Tables 4 and 5a.

EXAMPLE 3

Mineralised cement "C" was produced by adding gypsum and
20 fluorspar to the raw mix, burning the mixture in a production cement kiln, and grinding the clinker in a production cement mill circuit. No gypsum was added to the mill.

Ca. 40 kg batches of blended cements were prepared by mixing the base cement with various amounts of cement kiln electrostatic precipitator dust "M" (median grain size: 2.6 μm).
25 Mixing was carried out by agitating the materials in a rotating, rubber ball-containing steel drum.

The results of the investigation are shown in Table 6. It is notable that the strength contribution of cement kiln electrostatic precipitator dust "M" is significantly enhanced
30 after not only 1 day (cf. Examples 1 and 2), but also after 7

and 28 days when added to a mineralised cement ("C") with a fairly low S.R. (2.8).

EXAMPLE 4

Mineralised cement "D" was produced by adding gypsum and
5 fluorspar to the raw mix, burning the mixture in a production cement kiln, and grinding the clinker in a production cement mill circuit equipped with a high efficiency separator. No gypsum was added to the mill.

Base cements were mixed with various amounts of cement kiln
10 electrostatic precipitator dust "M" (median grain size: 2.6 μm). Cement kiln electrostatic precipitator dust "R" (median grain size: 12.2 μm , $\text{Na}_2\text{O}_{\text{eq}}$: 11.8% by weight) was added to some blends and hemihydrate to others. The hemihydrate was prepared by heating gypsum at 110°C for two days. Mixing was
15 for some blends (85-70% by weight mineralised cement) carried out according to the method described in Example 3, whilst the method described in Example 1 was used for the rest. Cross checking showed that the mixing method did not influence the results obtained.

20 As a reference, conventional Portland cement "Y" was used.

The results of the investigation are shown in Table 7. The enhanced strength-contributing effect of cement kiln electrostatic precipitator dust to both 1, 7 and 28 day strength when used in combination with a low-S.R. mineralised cement
25 ("D", S.R. = 2.6), and the surprisingly high strength at high amounts of added extender are clearly seen. Further 1-day strength increases were achieved by adding alkali (as cement kiln electrostatic precipitator dust "R") or sulfate (as hemihydrate) to the extended cement.

EXAMPLE 5

Mineralised cements "E" and "F" were produced by adding gypsum and fluorspar to the raw mix, and burning the mixture in a production cement kiln. Cement "E" was ground in a production cement mill circuit equipped with a high efficiency separator whereas cement "F" was ground in a production mill circuit without a high efficiency separator. No gypsum was added to the mill.

Ca. 5 kg batches of blended cements were prepared by mixing the base cement with various amounts of fine alumina "T" (median grain size: $1.1 \mu\text{m}$). Mixing was carried out by stirring the materials in a plastic container filled with rubber balls, using a shaking apparatus.

As a reference, conventional Portland cement "Y" was used.

These experiments were conducted in order to investigate whether fine-grain alumina might perform similarly to the fine carbonate-based extenders. The results (Table 8) show that this is not the case.

EXAMPLE 6

Mineralised cement "F" was produced as described in Example 5. Mineralised cement "G" was produced by adding fluorspar to the raw mix, burning the mixture in a production cement kiln, and grinding the clinker in a laboratory ball mill. 4% by weight of gypsum was added to the cement during grinding.

Ca. 5 kg batches of blended cements were prepared by mixing the base cement with various amounts of cement kiln electrostatic precipitator dust "M" (median grain size: $2.6 \mu\text{m}$). Mixing was carried out by stirring the materials in a plastic

container filled with rubber balls, using a shaking apparatus.

The results of the investigation are shown in Table 9. This example illustrates the effect of fine carbonate-based extender when used in combination with a mineralised cement of low LSF (Cement "F", LSF = 0.95) or with a mineralised cement which was produced by adding gypsum to the mill instead of to the kiln (cement "G"). It will be seen (Table 9) that the strength contribution of cement kiln electrostatic precipitator dust is significantly higher when added to these cements than when added to conventional Portland cement (see Table 7).

EXAMPLE 7

Mineralised cements were produced by adding gypsum and fluor-spar to the raw mix, burning the mixture in a production cement kiln, and grinding the clinker in a production cement mill circuit equipped with a high efficiency separator. No gypsum was added to the mill.

Blended cement "1" was produced by mixing cement kiln electrostatic precipitator dust "M" (median grain size: 2.6 μm) and mineralised cement "H" in the same manner as described in Example 3. Blended cements "2" and "3" were manufactured during a production trial, where cement kiln electrostatic precipitator dust similar to "M" was added to a mineralised cement similar to "E" in the high efficiency separator of a production mill circuit.

The blended cements were used to manufacture concretes. As reference, concretes were produced with the conventional Portland cement "Y".

Concrete recipes and mortar and concrete results are found in Table 10. The results show that extended cements with a per-

formance similar to that of laboratory-mixed cements may be produced on a large-scale installation. The example also shows that high concrete strengths may be attained by use of the extended cements. Comparison with strengths of concretes
5 made with conventional Portland cement indicates that the use of the extended cement containing 15% by weight of cement kiln electrostatic precipitator dust may make significant cement savings possible in concrete.

Table 1a: Base cement properties - 1

Cement type		Mineralised cement				
5	Designation	"A"	"B"	"C"	"D"	"E"
	Approx. quantity gypsum added to mill (% w/w)	0.0	0.0	0.0	0.0	0.0
10	Chemical Composition (% w/w)					
	SiO ₂	22.5	21.9	20.1	19.9	19.7
	Al ₂ O ₃	2.35	2.3	4.63	5.18	5.32
	Fe ₂ O ₃	0.87	1.0	2.65	2.58	2.85
	CaO	69.1	68.5	67.1	66.3	66.9
15	MgO	0.58	0.6	0.73	0.75	0.74
	SO ₃	2.70	3.48	2.55	2.28	2.50
	F	0.26	0.28	0.27	0.26	0.26
	LOI	0.80	0.9	0.85	0.49	0.46
	K ₂ O	0.37	0.33	0.46	0.62	0.58
20	Na ₂ O	0.23	0.20	0.24	0.27	0.24
	Na ₂ O _{eq}	0.47	0.42	0.54	0.68	0.62
	Free lime	1.38	1.26	1.76	2.49	1.59
	Ratios (w/w)					
	L.S.F.	1.01	1.02	1.03	1.02	1.03
25	A/F	2.7	2.3	1.8	2.0	1.9
	S.R.	7.0	6.6	2.8	2.6	2.4
	Bogue mineralogical composition (% w/w)					
30	C ₃ S	79.9	80.5	71.3	63.7	69.6
	C ₂ S	4.2	2.1	3.7	9.0	3.9
	C ₃ A	4.8	4.4	7.8	9.4	9.3
	C ₄ AF	2.5	3.0	8.1	7.9	8.7
	Density (kg/m ³)	3145	3114	3124	3152	
	Median grain size, d ₅₀ (μm)	15.0	13.8	11.8	14.0	10.4
35	Specific surface area (m ² /kg)	388	375	400	389	396
	Normal consistency (% w/w)	26.0	30.2	28.0	28.4	29.4
	Initial Set (h:min)	2:20	3:45	1:15	2:00	2:20
	Final set (h:min)	3:00	4:30	1:40	2:25	3:10
40	Compressive strength (MPa)					
	1 day	27.0	22.7	23.8	21.6	24.6
	7 days	56.5	62.0	57.8	56.0	57.6
	28 days	69.2	77.4	66.9	63.3	66.6

Table 1b: Base cement properties - 2

Cement type		Mineralised cement			Conventional Portland cement	
5	Designation	"F"	"G"	"H"	"X"	"Y"
10	Approx. quantity SO ₃ added as gypsum to mill (% w/w)	0.0	1.6 ^a	0.0	3.0 ^a	2.5 ^a
Chemical Composition (% w/w)						
15	SiO ₂	20.7	19.9	20.0	20.4	21.3
	Al ₂ O ₃	5.64	5.32	4.76	4.7	4.76
	Fe ₂ O ₃	3.30	3.09	2.71	3.0	2.85
	CaO	65.5	66.2	67.0	64.4	64.3
	MgO	0.77	0.74	0.75	0.8	0.75
20	SO ₃	2.48	2.22	2.65	3.5	3.10
	F	0.26	0.29	0.29	0.04	0.05
	LOI	0.17	1.07	0.36	1.30	1.37
	K ₂ O	0.61	0.53	0.45	0.53	0.53
	Na ₂ O	0.25	0.23	0.24	0.24	0.25
25	Na ₂ O _{eq}	0.65	0.58	0.54	0.59	0.60
	Free lime	0.57	1.54	1.62	1.1	1.54
Ratios (w/w)						
25	L.S.F.	0.95	1.01	1.03	0.96	0.93
	A/F	1.7	1.7	1.8	1.6	1.7
	S.R.	2.3	2.4	2.7	2.6	2.8
Bogue mineralogical composition (% w/w)						
30	C ₃ S	57.1	65.7	70.6	55.8	48.7
	C ₂ S	16.4	7.4	4.2	16.4	24.4
	C ₃ A	9.4	8.9	9.0	7.7	7.8
	C ₄ AF	10.0	9.4	8.3	9.2	8.7
35	Density (kg/m ³)	3247	3197	3120	3151	3118
	Median grain size, d ₅₀ (μm)	16.8	12.8	11.5	13.2	14.2
	Specific surface area (m ² /kg)	318	408	363	391	399
40	Normal consistency (% w/w)	25.3	26.4	29.7	28.6	28.0
	Initial Set (h:min)	2:40	1:45	2:05	2:30	1:50
	Final set (h:min)	3:35	2:25	2:40	3:00	2:15
	Compressive strength (MPa)					
	1 day	9.8	16.5	22.6	19.7	22.0
45	7 days	46.6	55.7	61.1	55.2	48.2
	28 days	66.0	62.4	70.9	62.7	63.3

^a No gypsum added to the kiln, clinker SO₃ content approx. 0.5-0.6% w/w

Table 2: Composition of extenders

Designation	Cement kiln electrosta- tic precipitator dust				Fine chalk
	"K"	"L"	"M"	"R"	"N"
5					
Chemical Composition					
(% w/w)					
SiO ₂	10.9	10.7	11.4	10.6	4.46
TiO ₂	0.19	0.13		0.06	
Al ₂ O ₃	2.62	2.25	2.71	0.97	0.70
Fe ₂ O ₃	1.74	1.52	1.18	0.36	0.22
CaO	46.2	47.2	47.1	30.4	52.0
MgO	0.46	0.42	0.46	0.29	0.33
SO ₃	0.64	0.40	1.21	20.3	0.15
F	0.04	0.04	0.12		0.05
LOI	35.6	35.8	34.3	19.0	41.7
K ₂ O	0.78	0.68	0.45	12.6	0.11
Na ₂ O	0.22	0.21	0.20	3.52	0.04
Na ₂ O _{eq}	0.73	0.66	0.49	11.8	0.11
Cl ₂ _{eq}	0.31	0.03	0.26		0.00
Free lime	0.13	1.23	2.02		
Density (kg/m ³)	2703	2706	2701	2664	2779
Median grain size, d ₅₀ (μm)	2.5	2.4	2.6	12.2	2.2
Specific surface					
area (m ² /kg)	1171	1199	1228	849	1421
25					

Designation	Coarse lime- stone	Coarse lime- stone	Fly ash	Blast fur- nace slag	Fine alumina		
5	"O"	"P"	"Q"	"S"	"T"		
<hr/>							
Chemical Composition							
10	(% w/w)	SiO ₂	3.70	1.52	56.2	33.9	0.15
		TiO ₂		0.04	0.99	0.48	
		Al ₂ O ₃	0.22	0.07	21.5	11.2	>99.6
		Fe ₂ O ₃	0.12	0.10	9.91	1.3	0.03
		CaO	52.7	54.7	3.15	41.9	0.02
15		MgO	0.70	0.26	1.73	9.2	0.1
		SO ₃	0.08	0.00	0.54	0.1	
		F		0.06			
		LOI	42.2	43.1	2.80	0.4	<0.5
		K ₂ O	0.05	0.01	2.16	0.29	
20		Na ₂ O	0.03	0.03	0.80	0.30	0.1
		Na ₂ O _{eq}	0.06	0.05	2.22	0.49	
		Cl ⁻	0.00			0.01	
		Free lime					
	<hr/>						
	Density (kg/m ³)	2733	2682	2277	2950	3980	
	Median grain size, d ₅₀ (μm)	12.0	9.6	19.0	11.0	1.1	
25	Specific surface area (m ² /kg)	509	521	255	426		

^a Manufacturer's data

Table 3: Mineralised or conventional Portland cement combined with various limestone-based extenders

<hr/>				
Composition (% w/w)				
5	Mineralised cement "A"	90	90	90
	Cem. kiln el. precipitator dust "K"	10		
	Fine chalk "N"		10	
	Coarse limestone "O"			10
10	Normal consistency (% w/w)	26.2	26.2	26.6
	Initial set (h:min)	3:10	3:05	3:15
	Final set (h:min)	3:30	3:40	3:40
Compressive strength absolute (MPa)/				
15	relative (%),			
	1 day	30.4/113	28.3/105	24.3/90
	7 days	55.7/99	53.8/95	49.3/87
	28 days	67.0/97	65.6/95	59.6/86
<hr/>				
20				
<hr/>				
Composition (% w/w)				
	Mineralised cement "A"	77	77	77
	Cem. kiln el. precipitator dust "K"	23		
25	Fine chalk "N"		23	
	Coarse limestone "O"			23
	Normal consistency (% w/w)	27.2	27.0	26.0
	Initial set (h:min)	2:05	2:35	2:45
	Final set (h:min)	2:30	3:00	3:10
30	Compressive strength absolute (MPa)/			
	relative (%),			
	1 day	28.9/107	26.1/97	21.5/80
	7 days	52.9/94	49.4/87	42.8/76
35	28 days	57.3/83	54.3/78	52.9/76
<hr/>				

<hr/>					
Composition (% w/w)					
5	Mineralised cement "A"	65	65		65
	Conventional Portland cement "X"			65	
	Cem. kiln el. precipitator dust "K"	35			
	Fine chalk "N"		35	35	
	Coarse limestone "O"				35
<hr/>					
10	Normal consistency (% w/w)	28.5	29.0	31.0	27.4
	Initial set (h:min)	1:55	2:10	1:55	2:00
	Final set (h:min)	2:45	2:25	2:50	2:40
<hr/>					
Compressive strength absolute (MPa)/					
15	relative (%),				
	1 day	24.7/91	21.3/79	13.4/68	17.1/63
	7 days	46.4/82	41.9/74	34.7/63	37.1/66
	28 days	51.9/75	44.3/64	43.5/69	41.9/61
<hr/>					

20 Table 4: Mineralised or conventional Portland cement combined with various limestone-based extenders

<hr/>					
Composition (% w/w)					
25	Mineralised cement "B"	85		85	
	Conventional Portland cement "X"		85		85
	Cem. kiln el. precipitator dust "L"	15	15		
	Coarse limestone "P"			15	15
<hr/>					
30	Normal consistency (% w/w)	30.2	29.0	29.6	29.0
	Initial set (h:min)	3:05	2:30	2:10	2:15
	Final set (h:min)	3:35	2:50	2:45	2:35
<hr/>					
Compressive strength absolute (MPa)/					
35	relative (%),				
	1 day	28.4/125	18.8/95	24.0/106	16.3/83
	7 days	60.3/97	50.6/91	59.0/95	46.9/85
	28 days	69.1/89	62.1/99	69.8/90	57.2/91
<hr/>					

<hr/>					
5	Composition (% w/w)				
	Mineralised cement "B"	75		75	
	Conventional Portland cement "X"		75		75
	Cem. kiln el. precipitator dust "L"	25	25		
	Coarse limestone "p"			25	25
	Normal consistency (% w/w)	31.0	30.2	28.0	27.2
10	Initial set (h:min)	3:05	2:10	2:45	2:00
	Final set (h:min)	3:45	2:50	3:20	2:25
15	Compressive strength absolute (MPa)/relative (%),				
	1 day	26.4/116	17.5/89	23.0/101	12.9/65
	7 days	55.4/89	43.8/79	51.6/83	39.1/71
	28 days	62.2/80	53.6/85	60.2/78	48.8/78
<hr/>					
20	Composition (% w/w)				
	Mineralised cement "B"	65		65	
	Conventional Portland cement "X"		65		65
25	Cem. kiln el. precipitator dust "L"	35	35		
	Coarse limestone "p"			35	35
	Normal consistency (% w/w)	31.0	31.2	27.6	27.0
	Initial set (h:min)	3:00	2:30	2:30	2:00
	Final set (h:min)	3:40	3:15	3:05	2:30
30	Compressive strength absolute (MPa)/relative (%),				
	1 day	23.9/105	13.9/71	18.7/82	10.6/54
	7 days	46.5/75	36.1/65	42.6/69	32.1/58
	28 days	53.9/70	45.8/73	48.6/63	41.7/67
35					
<hr/>					

**Table 5a: Mineralised or conventional Portland cement
combined with fly ash or ground granulated
blast furnace slag**

5	Composition (% w/w)				
	Mineralised cement "B"	80			
	Conventional Portland cement "X"		80		
	Fly ash "Q"	20	20		
10	Normal consistency (% w/w)	30.3	29.6		
	Initial set (h:min)	4:05	3:10		
	Final set (h:min)	4:50	4:40		
	Compressive strength absolute (MPa)/				
15	relative (%),				
	1 day	17.2/76	13.8/70		
	7 days	50.7/82	39.5/72		
	28 days	66.0/85	54.3/87		
20	Composition (% w/w)				
	Mineralised cement "B"	70		70	
	Conventional Portland cement "X"		70		70
25	Fly ash "Q"	30	30		
	Blast furnace slag "S"			30	30
	Normal consistency (% w/w)	29.1	28.0	31.2	29.2
	Initial set (h:min)	4:10	3:10	4:00	2:50
	Final set (h:min)	5:00	3:50	4:30	3:15
30	Compressive strength absolute (MPa)/				
	relative (%),				
	1 day	13.8/61	11.7/59	15.8/70	11.5/58
	7 days	40.9/66	32.8/59	46.1/74	40.1/73
35	28 days	54.3/70	44.4/71	66.3/106	61.5/98

Composition (% w/w)					
5	Mineralised cement "B"	60		60	
	Conventional Portland cement "X"		60		60
	Fly ash "Q"	40	40		
	Blast furnace slag "S"			40	40
Normal consistency (% w/w)					
10	Initial set (h:min)	28.8	28.6	32.4	29.0
	Final set (h:min)	4:45	3:20	4:00	2:35
		5:45	4:15	4:35	3:00
Compressive strength absolute (MPa)/relative (%)					
15	1 day	11.9/52	8.0/41	13.7/60	9.6/49
	7 days	33.8/55	24.5/44	42.2/68	37.2/60
	28 days	44.4/57	35.7/57	63.2/101	62.0/99

20 **Table 5b: Mineralised or conventional Portland cement combined with cement kiln electrostatic precipitator dust and fly ash or ground granulated blast furnace slag**

Composition (% w/w)					
25	Mineralised cement "B"	65		65	
	Conventional Portland cement "X"		65		65
	Cem. kiln electrostatic precipitator dust "L"	15	15	15	15
30	Fly ash "Q"	20	20		
	Blast furnace slag "S"			20	20
Normal consistency (% w/w)					
	Initial set (h:min)	29.2	28.2	30.0	31.0
	Final set (h:min)	3:30	2:50	3:05	2:50
		4:00	3:15	3:35	3:20
Compressive strength absolute (MPa)/relative (%)					
35	1 day	18.4/81	11.4/58	20.7/91	12.3/62
	7 days	46.1/74	34.6/63	51.0/82	44.1/80
	28 days	51.6/67	45.8/73	67.1/87	58.4/93

40

Table 6: Mineralised or conventional Portland cement combined with cement kiln electrostatic precipitator dust

5	Composition (% w/w)				
	Mineralised cement "C"	95	90	85	70
	Cem. kiln el. precipitator dust "M"	5	10	15	30
	Normal consistency (% w/w)	27.7	27.9	28.2	30.2
10	Initial set (h:min)	1:15	1:25	1:20	1:30
	Final set (h:min)	2:00	1:50	1:50	2:00
	Compressive strength absolute (MPa)/relative (%),				
15	1 day	23.9/100	25.9/109	25.8/108	22.0/92
	7 days	60.3/104	60.3/104	58.5/101	50.1/87
	28 days	70.8/106	67.1/100	63.7/95	57.6/86

Table 7: Mineralised or conventional Portland cement combined with cement kiln electrostatic precipitator dust

20	Composition (% w/w)				
	Mineralised cement "D"	85	80		75
25	Conventional Portland cement "Y"			80	
	Cem. kiln el. precipitator dust "M"	15	20	20	25
30	Compressive strength absolute (MPa)/relative (%),				
	1 day	24.0/111	24.2/112	19.1/87	24.0/111
	7 days	55.9/100	52.0/93	44.7/93	52.7/94
35	28 days	64.6/102	64.6/102		60.8/96

<hr/>					
Composition (% w/w)					
5	Mineralised cement "D"	70		65	60
	Conventional Portland cement "Y"		70		
Cem. kiln el. precipitator dust "M"					
		30	30	35	40
<hr/>					
Compressive strength absolute (MPa)/					
10	relative (%)				
	1 day	22.2/103	16.2/74	21.6/100	19.3/89
	7 days	50.1/89		45.9/82	42.0/75
	28 days	56.7/90		51.3/81	49.1/78
<hr/>					
15					
<hr/>					
Composition (% w/w)					
	Mineralised cement "D"	55	62	62	57
	Cem. kiln el. precipitator dust "M"	45	35	35	40
20	Cem. kiln el. precipitator dust "R"			3	3
	Hemihydrate		3		
<hr/>					
Compressive strength absolute (MPa)/					
25	relative (%)				
	1 day	18.0/83	25.3/117	23.6/109	22.2/103
	7 days	36.9/66	44.7/80	42.3/76	37.9/68
	28 days	44.6/70	51.7/82	47.0/74	44.1/70
<hr/>					
30 Table 8: Mineralised or conventional Portland cement combined with finely milled calcined alumina					
<hr/>					
Composition (% w/w)					
35	Mineralised cement "E"	80			
	Mineralised cement "F"		80		
	Conventional Portland cement "Y"			80	
Fine alumina "T"					
		20	20	20	
<hr/>					
Compressive strength absolute (MPa)/					
40	relative (%)				
	1 day	7.8/32	5.9/60	12.5/60	
	7 days	36.0/63	33.0/71	37.4/78	
<hr/>					

Table 9: Mineralised or conventional Portland cement combined with cement kiln electrostatic precipitator dust

5	Composition (% w/w)				
	Mineralised cement "F"	85	80	75	
	Mineralised cement "G"				80
	Cem. kiln el. precipitator dust "M"	15	20	25	20
10	Normal Consistency (% w/w)	26.4	26.7	27.2	
	Initial set (h/min)	2:40	2:20	2:15	
	Final set (h/min)	3:10	3:00	2:55	
	Compressive strength absolute (MPa)/				
15	relative (%),				
	1 day	12.9/132	11.5/117	11.7/119	17.8/108
	7 days	46.7/100	45.5/98	42.8/92	54.7/98

Table 10: Mineralised cement combined with cement kiln electrostatic precipitator dust

Concrete recipes (kg/m³)

		"I"	"II"
25	Cement	130	250
	Fly ash	50	
	Silica fume	14	
	Water	154	150
30	Sand	845	820
	Aggregate 4-8 mm	115	115
	Aggregate 8-16 mm	1030	1030
	Plasticizer	2	2

Results		"1"	"2"	"3"	Ref.
Designation					
5	Composition (% w/w) Mineralised cement similar to "E" Mineralised cement "H" Conventional Portland cement "Y"	85	85	75	100
10	Cem. kiln el. precipitator dust "M" Cem. kiln el. precipitator dust similar to "M"	15	15	25	
15	Compressive strength (EN 196-1 mortar) absolute (MPa), 1 day 7 days 28 days	24.6 54.4 65.4	26.2 55.1 67.6	21.6 51.3 58.2	22.0 48.2 63.3
20	Compressive strength (concrete "I") absolute (MPa), 1 day 7 days 28 days	2.8 13.3 22.6	2.0 13.3 23.2	1.6 10.9 19.2	2.5 8.9 18.8
30	Compressive strength (concrete "II") absolute (MPa), 1 day 7 days 28 days	7.9 31.4 37.0	7.0 34.5 37.7	8.9 27.7 32.4	8.2 24.4 32.8

CLAIMS

1. A cement composition consisting essentially of
 - a) from 50% to 97% by weight (calculated on the total composition) of a Portland cement clinker, the sulfur content of which is in the range of 0.5-10% by weight expressed as SO_3 , and the fluorine content of which is in the range of 0.13-1.00% by weight expressed as F^- ; and
 - b) from 3% to 50% by weight (calculated on the total composition) of an extender containing a carbonate selected from calcium carbonate, magnesium carbonate and calcium magnesium carbonate, and mixtures thereof, as its main constituent and having a median particle size (d_{50}) of below 14 μm .
2. A cement composition according to claim 1 wherein the median particle size (d_{50}) of the extender is below 12 μm , preferably below 10 μm , more preferably below 6 μm , in particular below 4 μm , especially below 3 μm .
3. A cement composition according to claim 1 or 2 wherein the extender is selected from carbonate-containing rocks, minerals or synthetic compounds such as calcite, aragonite, dolomite, limestone, dolostone, dolomitic limestone, travertine, calcarenite, coquina, chalk, marble, or industrial products, by-products or wastes containing such materials, or carbonate-containing electrostatic precipitator dust.
4. A cement composition according to any of claims 1-3 wherein the content of calcium carbonate, magnesium carbonate, calcium magnesium carbonate or mixtures thereof in the extender is at least 50%, preferably at least 60%, more preferably at least 70%, in particular at least 75%, more particularly at least 80% by weight, calculated on the extender.
5. A cement composition according to any of claims 1-4 wherein the content of Portland cement clinker and extender is 60-

95% and 5-40% by weight, respectively, preferably 65-95% and 5-35% by weight, respectively, in particular 70-90% and 10-30% by weight, respectively.

6. A cement composition according to any of claims 1-5 wherein the total content of C_3S and C_2S in the Portland cement clinker is at least 65%, preferably at least 70%, in particular at least 75%, especially at least 80%, calculated according to Bogue and corrected for the content of calcium sulfate in the clinker.
7. A cement composition according to any of claims 1-6 wherein the Portland cement clinker has a sulfur content in the range of 1.3-10% by weight expressed as SO_3 , and a fluorine content in the range of 0.13-0.55% by weight expressed as F^- .
8. A cement composition according to any of the preceding claims wherein the alkali metal content of the Portland cement clinker expressed as Na_2O equivalent is in the range of 0.1-8% by weight, preferably 0.2-0.7% by weight, more preferably 0.3-0.6% by weight.
9. A cement composition according to any of the preceding claims wherein the sulfur content of the Portland cement clinker expressed as SO_3 is in the range of 1.5-6% by weight, preferably 1.6-5%, in particular 1.8-4%.
10. A cement composition according to any of the preceding claims wherein the fluorine content of the Portland cement clinker expressed as F^- is in the range of 0.15-0.45% by weight, preferably 0.15-0.35%, in particular 0.18-0.30%.
11. A cement composition according to any of the preceding claims wherein the C_3S in the Portland cement clinker is of improved hydraulic activity and is present in the crystal modification characterized by the presence in the X-ray diffractogram of only one peak in the region 51° - 52° 2θ corresponding to the 220 reflection of the hexagonal subcell.

12. A cement composition according to any of the preceding claims in which fluorine in the Portland cement clinker is predominantly present in solid solution in the silicate crystal phases, preferably that at least 85%, in particular at least 95%, of the fluorine is present in solid solution in the silicate crystal phases.

13. A cement composition according to any of the preceding claims in which the Portland cement clinker contains more than 0.6% by weight, preferably more than 1.0% by weight, in particular more than 1.4% by weight, of aluminium in solid solution in the silicate crystal phases, expressed as Al_2O_3 .

14. A cement composition according to any of the preceding claims in which the Portland cement clinker has a lime saturation factor, corrected for the content of sulfate, of at least 0.95, preferably at least 0.97, in particular at least 0.99.

15. A cement composition according to any of the preceding claims wherein the silica ratio of the Portland cement clinker is in the range of 2-30, preferably 2-20.

16. A cement composition according to any of the preceding claims wherein the sulfur/fluorine ratio of the Portland cement clinker expressed as SO_3/F is at least 6.6, preferably at least 7, in particular at least 8.

17. A cement composition according to any of the preceding claims wherein the C_3S content of the Portland cement clinker is at least 60%, preferably at least 65%, in particular at least 70%, especially at least 75 % by weight.

18. A cement composition according to any of the preceding claims wherein the aluminium content of the Portland cement clinker expressed as Al_2O_3 is less than 6% by weight, preferably less than 5%.

19. A cement composition according to any of the preceding claims wherein the content of free lime in the Portland cement clinker is less than 3%, preferably less than 2% by weight.
- 5 20. A cement composition according to any of the preceding claims wherein the content of calcium langbeinite in the Portland cement clinker is in the range of 0.1-8.3%, preferably 0.1-6%, in particular 0.1-4% by weight.
- 10 21. A cement composition according to any of the preceding claims wherein the cement clinker is ground to a specific surface area according to Blaine of 150-1000 m²/kg, preferably 200-900 m²/kg.
22. A cement composition according to any of the preceding claims which further contains a retarding agent.
- 15 23. A cement composition according to claim 22 wherein the retarding agent is calcium sulfate or a hydrate thereof.
24. A cement composition according to any of the preceding claims wherein the extender has an alkali metal content of below 0.8% by weight expressed as Na₂O equivalent.
- 20 25. A cement composition according to any of the preceding claims which, when the cement clinker is ground to a specific surface area according to Blaine of 400 m²/kg, exhibits a 1-day compressive strength measured according to EN-196-1 of at least 21 Mpa, more preferably at least 24 MPa, in particular 25 at least 26 MPa, especially at least 28 MPa, such as 30 MPa.
26. A composition comprising a cement composition according to any of the claims 1-25 as well as one or more further components selected from the group consisting of cement extenders, aggregate, plasticizing and superplasticising 30 agents, accelerators, concrete retarders, air entraining agents, defoaming agents, freezing point decreasing agents,

adhesiveness improving agents, water repellants or water-proofing agents, expansion-promoting agents, corrosion inhibiting agents radiation shielding agents, thickeners and water.

- 5 27. A composition according to claim 26 wherein the cement extender is selected from silica fume, calcined clay, natural pozzolan, artificial pozzolan, iron blast furnace slag, alumino-silicate, amorphous silica, rock flour, alumina, fluorspar, or mixtures thereof.
- 10 28. A composition according to claim 26 wherein the aggregate is selected from sand, gravel, crushed stone, crushed rock, blast furnace slag, combustion slag, heavyweight aggregate, lightweight aggregate, or mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 93/00132

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C04B 7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB, A, 2055786 (BLUE CIRCLE INDUSTRIES LIMITED), 11 March 1981 (11.03.81) --	1-28
A	US, A, 4042408 (RANSOM JAMES MURRAY ET AL), 16 August 1977 (16.08.77) -----	1-28

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

2 July 1993

Date of mailing of the international search report

'13 -07- 1993

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

May Hallne

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

28/05/93

International application No.

PCT/DK 93/00132

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2055786	11/03/81	AT-B- 383340	25/06/87
		AU-B- 531866	08/09/83
		AU-A- 6068980	05/02/81
		BE-A- 884441	23/01/81
		CH-A- 646123	15/11/84
		DE-A,C- 3028323	26/02/81
		FR-A,B- 2462401	13/02/81
		JP-C- 1335975	11/09/86
		JP-A- 56037255	10/04/81
		JP-B- 61000299	07/01/86
		NL-A- 8004255	03/02/81
		SE-B,C- 448230	02/02/87
		SE-A- 8005365	12/03/81
US-A- 4042408	16/08/77	AU-B- 507232	07/02/80
		AU-A- 1266976	13/10/77
		BE-A- 888301	31/07/81
		CA-A- 1062735	18/09/79
		GB-A- 1498057	18/01/78
		SE-B,C- 445039	26/05/86
		SE-A- 7604134	18/10/76